

Functional relations for the density functional exchange and correlation functionals connecting functionals at three densities.

Daniel P. Joubert^{1, a)}

Centre for Theoretical Physics, University of the Witwatersrand, PO Wits 2050, Johannesburg, South Africa

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It is shown that the DFT exchange and correlation functionals satisfy

$$\begin{aligned}
0 = & \gamma E_{hx} [\rho_N] + 2E_c^\gamma [\rho_N] \\
& - \gamma E_{hx} [\rho_{N-1}^\gamma] - 2E_c^\gamma [\rho_{N-1}^\gamma] \\
& + 2 \int d^3 r' (\rho_{N-1}^0(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})) v^0([\rho_N]; \mathbf{r}) \\
& + \int d^3 r' (\rho_{N-1}^0(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})) \mathbf{r} \cdot \nabla v^0([\rho_N]; \mathbf{r}) \\
& + \int d^3 r' \rho_N(\mathbf{r}) \mathbf{r} \cdot \nabla v_c^\gamma([\rho_N]; \mathbf{r}) \\
& - \int d^3 r' \rho_{N-1}^\gamma(\mathbf{r}) \mathbf{r} \cdot \nabla v_c^\gamma([\rho_{N-1}^\gamma]; \mathbf{r}) \\
& - \int d^3 r' f^\gamma(\mathbf{r}) \mathbf{r} \cdot \nabla v_{hxc}^\gamma([\rho_N]; \mathbf{r}) \\
& - 2 \int d^3 r' f^\gamma(\mathbf{r}) v_{hxc}^\gamma([\rho_N]; \mathbf{r})
\end{aligned}$$

In the derivation of this equation the adiabatic connection formulation is used where the ground state density of an N -electron system, ρ_N , is kept constant independent of the electron-electron coupling strength γ . Here $E_{hx}[\rho]$ is the Hartree plus exchange energy, $E_c^\gamma[\rho]$ is the correlation energy, $v_{hxc}^\gamma[\rho]$ is the Hartree plus exchange-correlation potential, $v_c[\rho]$ is the correlation potential and $v^0[\rho]$ is the Kohn-Sham potential. The charge densities ρ_N and ρ_{N-1}^γ are the N - and $(N-1)$ -electron ground state densities of the same Hamiltonian at electron-electron coupling strength γ . $f^\gamma(\mathbf{r}) = \rho_N(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})$ is the Fukui function. This equation can be useful in testing the internal self-consistency of approximations to the exchange and correlation functionals.

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Density Functional Theory (DFT)¹ is one of the most important tools for the calculation of electronic structure and structural properties of molecules and solids. In all practical applications of DFT, however, approximations to the exact functionals have to be used²⁻⁶. Exact relations for density functionals and density functional derivatives can play an important role in the development of accurate approximations to the exact functionals. A successful approach to the design of improved approximate density functionals is by 'constraint satisfaction'⁷, where the approximate functionals are required to satisfy properties of the exact functionals. The accuracy of approximate functionals can be tested by comparing to accurate calculations or to experimental data. A useful additional test will be to determine the internal self-consistency of approximations. With this in mind, the

following expression is derived:

$$\begin{aligned}
0 = & \gamma E_{hx} [\rho_N] + 2E_c^\gamma [\rho_N] \\
& - \gamma E_{hx} [\rho_{N-1}^\gamma] - 2E_c^\gamma [\rho_{N-1}^\gamma] \\
& + 2 \int d^3 r' (\rho_{N-1}^0(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})) v^0([\rho_N]; \mathbf{r}) \\
& + \int d^3 r' (\rho_{N-1}^0(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})) \mathbf{r} \cdot \nabla v^0([\rho_N]; \mathbf{r}) \\
& + \int d^3 r' \rho_N(\mathbf{r}) \mathbf{r} \cdot \nabla v_c^\gamma([\rho_N]; \mathbf{r}) \\
& - \int d^3 r' \rho_{N-1}^\gamma(\mathbf{r}) \mathbf{r} \cdot \nabla v_c^\gamma([\rho_{N-1}^\gamma]; \mathbf{r}) \\
& - \int d^3 r' f^\gamma(\mathbf{r}) \mathbf{r} \cdot \nabla v_{hxc}^\gamma([\rho_N]; \mathbf{r}) \\
& - 2 \int d^3 r' f^\gamma(\mathbf{r}) v_{hxc}^\gamma([\rho_N]; \mathbf{r})
\end{aligned} \tag{1}$$

In the derivation of this expression the adiabatic connection formulation⁸⁻¹¹ is used where the ground state density of an N -electron system, ρ_N , is kept constant

^{a)}Electronic mail: daniel.joubert2@wits.ac.za

independent of the electron-electron coupling strength γ . In Eq.(1) $v_{hxc}^\gamma[\rho]$ is the Hartree plus exchange-correlation potential, $v_c[\rho]$ is the correlation potential and $v^0[\rho]$ is the Kohn-Sham potential. $E_c^\gamma[\rho]$ is the correlation energy while $E_{hx}[\rho]$ is the Hartree plus exchange energy. The charge densities ρ_N and ρ_{N-1}^γ are the N - and $(N-1)$ -electron ground state densities of the same Hamiltonian at electron-electron coupling strength γ as discussed below. $f^\gamma(\mathbf{r}) = \rho_N(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})$ is the Fukui function.

Equation (1) couples functionals and functional derivatives evaluated at three different densities and two particle numbers. This equation can be used as a stringent test to check the internal self-consistency of approximations to the exchange and correlation functionals. If exact exchange is used it can serve as a check on approximations to the correlation energy functional.

Evaluation of (1) requires two independent self-consistent Kohn-Sham calculations, one for the N -electron system to determine ρ_N and ρ_{N-1}^0 , and one for the $(N-1)$ -electron system to determine ρ_{N-1}^γ . Once the densities are found, the functionals and functional derivatives can be used in Eq.(1) as a test of how well the approximations work.

I. PROOF OF EQUATION (1)

According to the Hohenberg-Kohn theorem¹ and its generalization to degenerate states¹² the ground state energy $E^\gamma[\rho]$ of a system of interacting electrons is a functional of ρ , the ground state density^{13,14}.

$$E^\gamma[\rho] = T^\gamma[\rho] + \gamma V_{ee}^\gamma[\rho] + \int d^3r \rho(\mathbf{r}) v^\gamma([\rho]; \mathbf{r}) \quad (2)$$

where $T^\gamma[\rho]$ is the kinetic energy and $\gamma V_{ee}^\gamma[\rho]$ the mutual Coulomb interaction energy at density ρ . In order to derive Eq.(1) the adiabatic connection approach will be used⁸⁻¹¹ in which the external potential $v_{\text{ext}}^\gamma([\rho]; \mathbf{r})$ is constructed to keep the ground state density independent of the electron-electron interaction strength, scaled by γ , and has the form^{15,16}

$$v^\gamma([\rho]; \mathbf{r}) = (1 - \gamma) v_{hx}([\rho]; \mathbf{r}) + v_c^1([\rho]; \mathbf{r}) - v_c^\gamma([\rho]; \mathbf{r}) + v_{\text{ext}}(\mathbf{r}). \quad (3)$$

$v^1([\rho]; \mathbf{r}) = v_{\text{ext}}(\mathbf{r})$ is the external potential at full coupling strength, $\gamma = 1$, and $v^0([\rho]; \mathbf{r})$ is non-interacting Kohn-Sham potential. The exchange plus Hartree potential^{13,14} $v_{hx}([\rho]; \mathbf{r})$, is independent of γ , while the correlation potential $v_c^\gamma([\rho]; \mathbf{r})$ depends in the scaling parameter γ . The adiabatically scaled N -electron Hamiltonian \hat{H}^γ has the form⁸⁻¹¹

$$\hat{H}^\gamma = \hat{T} + \gamma \hat{V}_{ee} + \hat{v}^\gamma[\rho]. \quad (4)$$

Atomic units, $\hbar = e = m = 1$ are used throughout. \hat{T} is the kinetic energy operator,

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2, \quad (5)$$

and $\gamma \hat{V}_{ee}$ is a scaled electron-electron interaction,

$$\gamma \hat{V}_{ee} = \gamma \sum_{i < j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (6)$$

and

$$\hat{v}^\gamma[\rho] = \sum_{i=1}^N v^\gamma[\rho]; \mathbf{r}_i. \quad (7)$$

Define the energy functional^{13,14}

$$\begin{aligned} F^\gamma[\rho] &= T^\gamma[\rho] + \gamma V_{ee}^\gamma[\rho] \\ &= T^0[\rho] + \gamma E_{hx}[\rho] + E_c^\gamma[\rho] \end{aligned} \quad (8)$$

where $E_{hx}[\rho]$ is the Hartree plus exchange energy, and $E_c^\gamma[\rho]$ is the correlation energy. Note that $E_{hx}[\rho]$ is independent of γ . As shown in appendix A

$$\begin{aligned} \mu &= v^\gamma(\mathbf{r}) + \frac{1}{2} \mathbf{r} \cdot \nabla v^\gamma(\mathbf{r}) + \frac{1}{2} (v_{hxc}^\gamma(\mathbf{r}) - t_c^\gamma(\mathbf{r})) \\ &\quad - \frac{1}{2} \int d^3r' \rho(\mathbf{r}') \mathbf{r}' \cdot \nabla' \frac{\delta^2 F^\gamma[\rho]}{\delta \rho(\mathbf{r}') \delta \rho(\mathbf{r})}, \end{aligned} \quad (9)$$

where $t_c^\gamma([\rho]; \mathbf{r}) = \frac{\delta T_c^\gamma[\rho]}{\delta \rho(\mathbf{r})}$ with $T_c^\gamma[\rho]$ the correlation part of the kinetic energy and $v_{hxc}^\gamma(\mathbf{r}) = \gamma v_{hx}(\mathbf{r}) + v_c^\gamma(\mathbf{r})$. For notational convenience the functional dependence on ρ has been suppressed. The chemical potential μ depends on the asymptotic decay of the charge density^{17,18}, and hence, since the charge density ρ is independent of γ by construction, μ is independent of γ .

The Fukui function^{19,20}

$$f^\gamma(\mathbf{r}) = \left. \frac{\delta \mu}{\delta v^\gamma(\mathbf{r})} \right|_N = \left. \frac{\delta \rho(\mathbf{r})}{\delta N} \right|_{v^\gamma} \quad (10)$$

satisfies

$$\int d^3r' \frac{\delta^2 F^\gamma[\rho]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} f^\gamma(\mathbf{r}') = \left. \frac{\partial \mu}{\partial N} \right|_{v^\gamma} \quad (11)$$

and

$$\int d^3r' f^\gamma(\mathbf{r}') = 1. \quad (12)$$

Since

$$\int d^3r' (3\rho(\mathbf{r}') + \mathbf{r}' \cdot \nabla \rho(\mathbf{r}')) = 0, \quad (13)$$

it follows from (9), (11) and (12) that

$$\begin{aligned} \mu &= \int d^3r' f^\gamma(\mathbf{r}) v^\gamma(\mathbf{r}) + \frac{1}{2} \int d^3r' f^\gamma(\mathbf{r}) \mathbf{r} \cdot \nabla v^\gamma(\mathbf{r}) + \\ &\quad \frac{1}{2} \int d^3r' f^\gamma(\mathbf{r}) (v_{hxc}^\gamma(\mathbf{r}) - t_c^\gamma(\mathbf{r})). \end{aligned} \quad (14)$$

Using (3), this equation can be reduced to

$$\begin{aligned} & \int d^3r' f^\gamma(\mathbf{r}) [2v^0(\mathbf{r}) + \mathbf{r} \cdot \nabla v^0(\mathbf{r})] - 2\mu \\ &= \int d^3r' f^\gamma(\mathbf{r}) \mathbf{r} \cdot \nabla v_{hxc}^\gamma(\mathbf{r}) \\ &+ \int d^3r' f^\gamma(\mathbf{r}) [v_{hxc}^\gamma(\mathbf{r}) + t_c^\gamma(\mathbf{r})]. \end{aligned} \quad (15)$$

From the virial theorem for the Kohn-Sham independent particle wavefunctions²¹

$$\begin{aligned} & \int d^3r' [\rho_N(\mathbf{r}) - \rho_{N-1}^0(\mathbf{r})] [2v^0(\mathbf{r}) + \mathbf{r} \cdot \nabla v^0(\mathbf{r})] \\ &= 2(E^0[\rho] - E^0[\rho_{N-1}^0]), \end{aligned} \quad (16)$$

where $E^0[\rho]$ and $E^0[\rho_{N-1}^0]$ are the Kohn-Sham ground state energies of the independent N - and $(N-1)$ -particle systems of the same Kohn-Sham Hamiltonian with potential v^0 . By definition, since μ is independent of γ ^{17,18},

$$\mu = E^\gamma[\rho] - E^\gamma[\rho_{N-1}^\gamma] \quad (17)$$

where $E^\gamma[\rho_N]$ and $E^\gamma[\rho_{N-1}^\gamma]$ are the ground state energies of the N - and $(N-1)$ -particle systems of the same Hamiltonian H^γ , Eq. (4), with ρ_N and ρ_{N-1}^γ the corresponding ground state densities. By construction $\rho_N^\gamma = \rho_N$ is independent of γ but ρ_{N-1}^γ is expected to be a function of γ .

Since the Fukui function^{22,23}

$$\begin{aligned} f^\gamma(\mathbf{r}) &= \left. \frac{\delta \rho(\mathbf{r})}{\delta N} \right|_{v^\gamma} \\ &= \rho_N(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r}) \end{aligned} \quad (18)$$

is the difference between the ground state densities of the N - particle and $(N-1)$ -particle systems, it follows from (15), (16) and (17), that

$$\begin{aligned} & 2 \int d^3r' (\rho_{N-1}^0(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})) v^0(\mathbf{r}) + \\ &+ \int d^3r' (\rho_{N-1}^0(\mathbf{r}) - \rho_{N-1}^\gamma(\mathbf{r})) \mathbf{r} \cdot \nabla v^0(\mathbf{r}) \\ &= \int d^3r' f^\gamma(\mathbf{r}) \mathbf{r} \cdot \nabla v_{hxc}^\gamma(\mathbf{r}) \\ &+ \int d^3r' f^\gamma(\mathbf{r}) [v_{hxc}^\gamma(\mathbf{r}) + t_c^\gamma(\mathbf{r})] \end{aligned} \quad (19)$$

The reference to the correlation part of the kinetic energy can be eliminated as follows. Since¹⁵

$$\gamma V_{ee}^\gamma[\rho] = \gamma E_{hx}[\rho] + E_c^\gamma[\rho] - T_c^\gamma[\rho], \quad (20)$$

the last line in (19) can be written as

$$\begin{aligned} & \int d^3r' f^\gamma(\mathbf{r}) [v_{hxc}^\gamma(\mathbf{r}) + t_c^\gamma(\mathbf{r})] \\ &= -\gamma \int d^3r' f^\gamma(\mathbf{r}) \frac{\delta V_{ee}^\gamma[\rho]}{\delta \rho(\mathbf{r})} \\ &+ 2 \int d^3r' f^\gamma(\mathbf{r}) v_{hxc}^\gamma(\mathbf{r}) \end{aligned} \quad (21)$$

As shown in appendix B²⁴,

$$\int d^3r' f^\gamma(\mathbf{r}) \frac{\delta V_{ee}^\gamma[\rho_N]}{\delta \rho_N(\mathbf{r})} = V_{ee}^\gamma[\rho_N] - V_{ee}^\gamma[\rho_{N-1}^\gamma]. \quad (22)$$

Since¹⁵

$$E_c^\gamma[\rho] + T_c^\gamma[\rho] = - \int d^3r' \rho(\mathbf{r}) \mathbf{r} \cdot \nabla [v_c^\gamma([\rho]; \mathbf{r})], \quad (23)$$

it follows from (20), (21), (22) and (23) that

$$\begin{aligned} & \int d^3r' f^\gamma(\mathbf{r}) [v_{hxc}^\gamma(\mathbf{r}) + t_c^\gamma(\mathbf{r})] \\ &+ \int d^3r' \rho_N(\mathbf{r}) \mathbf{r} \cdot \nabla v_c^\gamma([\rho_N]; \mathbf{r}) \\ &- \int d^3r' \rho_{N-1}^\gamma(\mathbf{r}) \mathbf{r} \cdot \nabla v_c^\gamma([\rho_{N-1}^\gamma]; \mathbf{r}) \\ &= \gamma E_{hx}[\rho_{N-1}^\gamma] + 2E_c^\gamma[\rho_{N-1}^\gamma] \\ &- \gamma E_{hx}[\rho_N] - 2E_c^\gamma[\rho_N] \\ &+ 2 \int d^3r' f^\gamma(\mathbf{r}) v_{hxc}^\gamma(\mathbf{r}). \end{aligned} \quad (24)$$

Combining (19) and (24) leads to Equation (1).

This equation is now entirely in terms of the exchange and correlation energy and potentials and other known density dependent quantities.

II. DISCUSSION AND SUMMARY

Equation(1) is valid for pure state DFT^{13,14} since equations (16) and (22) have been shown to be correct for pure states. Throughout it was assumed that the functionals derivatives are well defined^{13,14,25}.

Note that $\rho_{N-1}^\gamma \neq \rho_{N-1}^0$. In order to determine ρ_{N-1}^γ a Kohn-Sham calculation with²⁶

$$v^0[\rho_{N-1}^\gamma] = v^\gamma[\rho_N] + \gamma v_{hx}[\rho_{N-1}^\gamma] + v_c^\gamma[\rho_{N-1}^\gamma]$$

has to be performed. Note that $v^\gamma[\rho_{N-1}^\gamma] = v^\gamma[\rho_N]$.

In summary, an equation that couples exchange and correlation functionals and functional derivatives evaluated at three different densities and for two particle numbers has been derived. This equation can be used as a stringent test to check the internal self-consistency of approximations to the exchange and correlation functionals.

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Appendix A: Derivation of Eq. (9)

Let $\rho_\lambda(\mathbf{r}) = \lambda^3 \rho(\lambda \mathbf{r})$, the uniformly scaled density. Then (see for example Eq.(A.33) in Appendix A of reference¹³),

$$\begin{aligned} & \left. \frac{d}{d\lambda} \frac{\delta F^\gamma[\rho_\lambda]}{\delta \rho_\lambda(\mathbf{r})} \right|_{\rho_\lambda, \lambda=1} \\ &= \int d^3 r' (3\rho(\mathbf{r}') + \mathbf{r}' \cdot \nabla' \rho(\mathbf{r}')) \frac{\delta^2 F^\gamma[\rho]}{\delta \rho(\mathbf{r}') \delta \rho(\mathbf{r})} \\ &= - \int d^3 r' \rho(\mathbf{r}') \mathbf{r}' \cdot \nabla' \frac{\delta^2 F^\gamma[\rho]}{\delta \rho(\mathbf{r}') \delta \rho(\mathbf{r})}. \end{aligned} \quad (\text{A1})$$

The last line is valid if $\rho(\mathbf{r}')$ vanishes when $r \rightarrow \infty$ as would be the case for a finite system. Now consider the Schrödinger equation

$$\begin{aligned} & \left[-\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \frac{\gamma}{\lambda} \sum_{i<j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N v^{\frac{\gamma}{\lambda}}([\rho]; \mathbf{r}_i) \right] \Psi^{\frac{\gamma}{\lambda}}(\{\mathbf{r}_i\}) \\ &= E^{\frac{\gamma}{\lambda}}(v^{\frac{\gamma}{\lambda}}[\rho]) \Psi^{\frac{\gamma}{\lambda}}(\{\mathbf{r}_i\}) \end{aligned} \quad (\text{A2})$$

from which it follows that

$$\begin{aligned} & \left[-\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \gamma \sum_{i<j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N \lambda^2 v^{\frac{\gamma}{\lambda}}([\rho]; \mathbf{r}_i) \right] \Psi^{\frac{\gamma}{\lambda}}(\{\lambda \mathbf{r}_i\}) \\ &= \lambda^2 E^{\frac{\gamma}{\lambda}}(v^{\frac{\gamma}{\lambda}}[\rho]) \Psi^{\frac{\gamma}{\lambda}}(\{\lambda \mathbf{r}_i\}). \end{aligned} \quad (\text{A3})$$

If normalised $\Psi^{\frac{\gamma}{\lambda}}(\{\mathbf{r}_i\})$ yields $\rho(\mathbf{r})$ then normalised $\Psi^{\frac{\gamma}{\lambda}}(\{\lambda \mathbf{r}_i\})$ yields $\lambda^3 \rho(\lambda \mathbf{r})$. The Levy constrained minimization approach¹² implies that normalised $\Psi^{\frac{\gamma}{\lambda}}(\{\lambda \mathbf{r}_i\})$ yields $\lambda^3 \rho(\lambda \mathbf{r})$ and minimizes $\langle \Psi | \hat{T} + \gamma \hat{V}_{ee} | \Psi \rangle_{\Psi \rightarrow \lambda^3 \rho(\lambda \mathbf{r})}$.

Therefore^{13-15,27} $v^\gamma([\rho_\lambda]; \mathbf{r}) = \lambda^2 v^{\frac{\gamma}{\lambda}}([\rho]; \lambda \mathbf{r})$ and

$$\frac{\delta F^\gamma[\rho_\lambda]}{\delta \rho_\lambda(\mathbf{r})} + \lambda^2 v^{\frac{\gamma}{\lambda}}([\rho]; \lambda \mathbf{r}) = \mu_\lambda^\gamma, \quad (\text{A4})$$

and

$$\begin{aligned} & \left. \frac{d}{d\lambda} v^\gamma([\rho_\lambda]; \mathbf{r}) \right|_{\lambda=1} \\ &= 2v^\gamma([\rho]; \mathbf{r}) + \mathbf{r} \cdot \nabla v^\gamma([\rho]; \mathbf{r}) - \frac{\partial}{\partial \gamma} v^\gamma([\rho]; \mathbf{r}) \end{aligned} \quad (\text{A5})$$

For an N -electron system,

$$\mu_{N,\lambda}^\gamma = E_N^\gamma(\lambda^2 v^{\frac{\gamma}{\lambda}}[\rho]) - E_{N-1}^\gamma(\lambda^2 v^{\frac{\gamma}{\lambda}}[\rho]) \quad (\text{A6})$$

with $E_N^\gamma(\lambda^2 v^{\frac{\gamma}{\lambda}}[\rho_N])$ and $E_{N-1}^\gamma(\lambda^2 v^{\frac{\gamma}{\lambda}}[\rho_N])$ the groundstate energies of the N - and $(N-1)$ - electron systems with the same external potential $\lambda^2 v^{\frac{\gamma}{\lambda}}[\rho]$. From Eq.(A3) it follows that

$$\begin{aligned} \mu_{N,\lambda}^\gamma &= E_N^\gamma(\lambda^2 v^{\frac{\gamma}{\lambda}}[\rho]) - E_{N-1}^\gamma(\lambda^2 v^{\frac{\gamma}{\lambda}}[\rho]) \\ &= \lambda^2 (E_N^{\frac{\gamma}{\lambda}}(v^{\frac{\gamma}{\lambda}}[\rho]) - E_{N-1}^{\frac{\gamma}{\lambda}}(v^{\frac{\gamma}{\lambda}}[\rho])) \\ &= \lambda^2 \mu \end{aligned} \quad (\text{A7})$$

where the last step follows from the definition of the chemical potential of the N -electron system. Note that the chemical potential μ is independent of $\gamma^{17,18}$.

The correlation energy $E_c^\gamma[\rho]$ is defined as¹³⁻¹⁵

$$\begin{aligned} E_c^\gamma[\rho] &= \langle \Psi_\rho^\gamma | \hat{T} + \gamma \hat{V}_{ee} | \Psi_\rho^\gamma \rangle \\ &\quad - \langle \Psi_\rho^0 | \hat{T} + \gamma \hat{V}_{ee} | \Psi_\rho^0 \rangle, \end{aligned} \quad (\text{A8})$$

where $|\Psi_\rho^\gamma\rangle$ is the ground state wavefunction of H^γ that yields ρ and $|\Psi_\rho^0\rangle$ the Kohn-Sham independent N -electron groundstate wavefunction that yields the same density. The correlation part of the kinetic energy is given by

$$T_c^\gamma[\rho] = \langle \Psi_\rho^\gamma | \hat{T} | \Psi_\rho^\gamma \rangle - \langle \Psi_\rho^0 | \hat{T} | \Psi_\rho^0 \rangle, \quad (\text{A9})$$

and $\gamma V_{ee}^\gamma[\rho]$ ¹³⁻¹⁵ can be written as

$$\gamma V_{ee}^\gamma[\rho] = \gamma E_{hx}[\rho] + E_c^\gamma[\rho] - T_c^\gamma[\rho], \quad (\text{A10})$$

where $E_{hx}[\rho]$ is the sum of the Hartree and exchange energies. Note that $E_{hx}[\rho]$ is independent of γ . It follows from (A8) and (A9) that

$$t_c^\gamma(\mathbf{r}) + \gamma \frac{d}{d\gamma} v_c^\gamma(\mathbf{r}) - v_c^\gamma(\mathbf{r}) = 0, \quad (\text{A11})$$

where $t_c^\gamma([\rho]; \mathbf{r}) = \frac{\delta T_c^\gamma[\rho]}{\delta \rho(\mathbf{r})}$ and $v_c^\gamma([\rho]; \mathbf{r}) = \frac{\delta E_c^\gamma[\rho]}{\delta \rho(\mathbf{r})}$. Combining (3), (A1), (A4), (A5), (A7) and (A11) yields Eq. (9).

Appendix B: Derivation of Eq. (22)

Multiply Eq.(9) by the Fukui function and integrate over \mathbf{r} . Use Eq.(11), the fact that

$$\int d^3 r' (3\rho(\mathbf{r}') + \mathbf{r} \cdot \nabla \rho(\mathbf{r}')) = 0 \quad (\text{B1})$$

and Eq.(A11) to arrive at

$$\begin{aligned} & \int d^3 r' [2v^\gamma([\rho]; \mathbf{r}') + \mathbf{r} \cdot \nabla v^\gamma([\rho]; \mathbf{r}')] f^\gamma(\mathbf{r}) + \\ & \int d^3 r' [\gamma v_{hx}([\rho]; \mathbf{r}') + v_c^\gamma([\rho]; \mathbf{r}') - t_c^\gamma([\rho]; \mathbf{r}')] f^\gamma(\mathbf{r}') \\ &= 2\mu. \end{aligned} \quad (\text{B2})$$

From the definition of $E_c^\gamma[\rho]$ and $E_c^\gamma[\rho]$, Eqs. (A8) and (A9) and the fact that

$$E_{hx}[\rho] = \left\langle \Psi_\rho^0 \left| \hat{V}_{ee} \right| \Psi_\rho^0 \right\rangle, \quad (\text{B3})$$

it follows that

$$\gamma \frac{\delta V_{ee}^\gamma[\rho]}{\delta \rho(\mathbf{r})} = \gamma v_{hx}([\rho]; \mathbf{r}) + v_c^\gamma([\rho]; \mathbf{r}) - t_c^\gamma([\rho]; \mathbf{r}). \quad (\text{B4})$$

Using the virial theorem¹⁵ and $\mu = E^\gamma[\rho_N] - E^\gamma[\rho_{N-1}^\gamma]$,

$$\begin{aligned} & \int d^3r' [2v^\gamma([\rho]; \mathbf{r}') + \mathbf{r} \cdot \nabla v^\gamma([\rho]; \mathbf{r})] f^\gamma(\mathbf{r}) \\ &= 2\mu - \gamma V_{ee}^\gamma[\rho_N] + \gamma V_{ee}^\gamma[\rho_{N-1}^\gamma]. \end{aligned} \quad (\text{B5})$$

Combining Eq. (B2), (B4) and (B5) yields Eq. (22). For a detailed discussion see reference²⁴.

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